Basic Statistical Mechanics
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Lecture – 23
Ideal Gas of Diatomic Molecules: Microscopic Expression for Rotational and Vibrational Entropy and Specific Heat (Part 1)

In the morning, we did the monatomic gases and I will come back there is one part we did not do which is lot of fun. We will come back to that, but I just want to start fresh with the diatomic gases which has a huge number of very important results that we use in everyday in statistical mechanics in liquids and gases and solids. And you will see that monatomic gas results are used also in the diatomic gases; that is one of the reason I want to straight go there and get those things done to get started.

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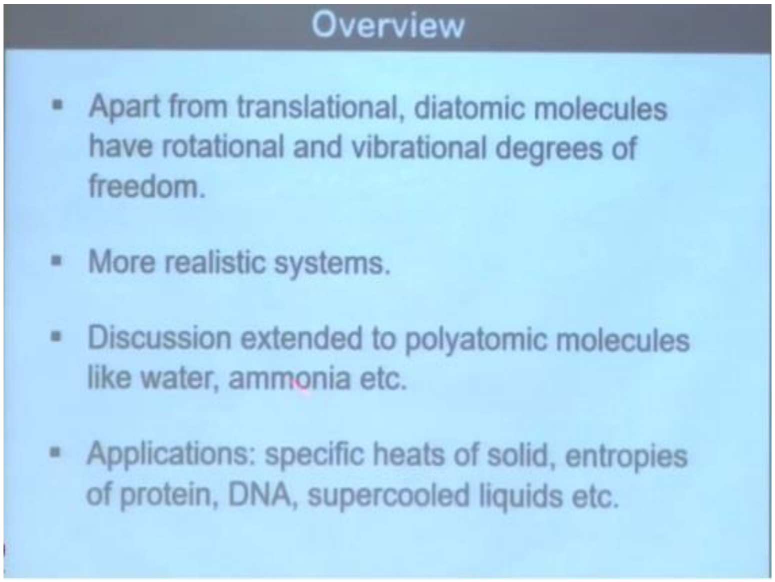

Overview

- Apart from translational, diatomic molecules have rotational and vibrational degrees of freedom.
- More realistic systems.
- Discussion extended to polyatomic molecules like water, ammonia etc.
- Applications: specific heats of solid, entropies of protein, DNA, supercooled liquids etc.

Okay, so there are diatomic gases of these additional degrees of freedom not just translation. We have rotational and vibrational degrees of freedom. Important difference now is that while translational degrees of freedom by a large accept at very low temperature can be treated classically, vibration cannot be treated classically, vibration degrees of freedom except some cases and we will discuss like normal modes, very soft modes a low frequency modes.

And the vibration that we see in molecules that cannot be treated classically, rotation is on the borderline and you are better doing it quantum mechanically. And they are the most realistic things because as we say diatomic gases are essentially noble gases but most of the other molecules that nitrogen, oxygen and all these things are diatomic. So this discussion today we will do will be extended to polyatomic molecules like water and ammonia.

We will discuss a lot of things in water and ammonia which will be very, very important and then applications will do specifically to solid, entropies okay these are applications we will not do too much of that, but we will mention them how these things go in. It is equations will derive today are used in understanding glasses**,** understanding proteins and DNA in a very, very well-known examples.

And these are what are the true many body systems which we usually in our chemistry vocabulary which is so much saddled with individual atoms and molecules and quantum chemical calculation of them, we hardly do many body phenomena. But when you do many body phenomena where many particles that interact with each other to give such phenomenon as phase transition, we need to do this interacting much body systems.

However, before you do the interacting many body systems, we need to understand non-interacting many body systems. In the morning we did monatomic gases and now we are going diatomic gases and diatomic gases introduced many profoundly important concepts which will again; will be used in many, many cases many, many applications; these are just some of them which we will now go to.

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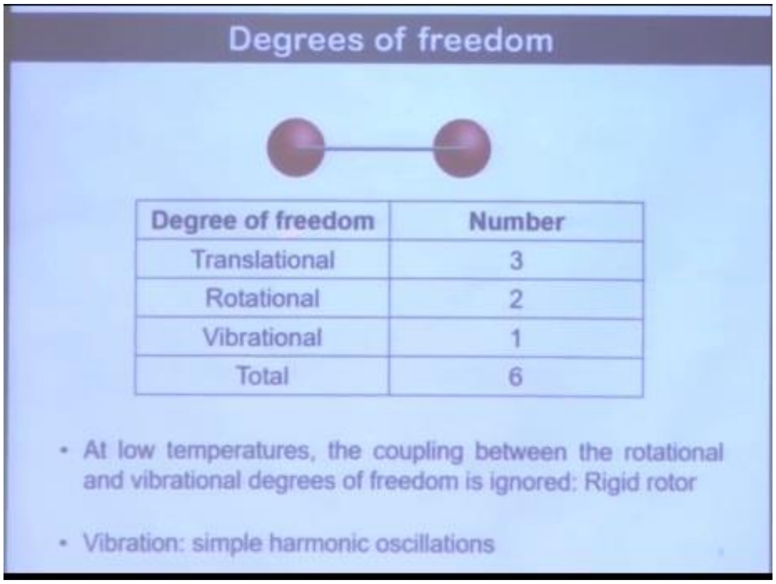

Degrees of freedom

Degree of freedom	Number
Translational	3
Rotational	2
Vibrational	1
Total	6

- At low temperatures, the coupling between the rotational and vibrational degrees of freedom is ignored: Rigid rotor
- Vibration: simple harmonic oscillations

Okay, as I said it is very important after preliminary things, things will get more mathematical but nothing very difficult. So remember that if you have such a diatomic molecule then degrees of freedom there is a three translational degrees of freedom, we model by the center of mass then two rotational degrees of freedom and 1 vibrational degrees of freedom total is six for two atoms. So then when you have a high temperature when the molecule rotating very fast there is a coupling between rotation and vibration that comes in.

What is the name of the coupling? You have done that in your undergraduate. Remember the QR branch of spectroscopy, huge amount of things done by Moore and Castellan You know, have some interest for god sake; this is a very nice important things, because they give huge amount of molecular information.

Okay, that because these are called Coriolis coupling and also some other forms of coupling that comes when; for example, a molecule rotates very fast then the bond, another is centrifugal, so there are two things that come in will rotate very fast then the bond can get stretched and that; goes at the called anharmonic effects. But at low temperatures we can low temperature these things can be ignored.

So we can have approximate low temperature by rigid rotator which is much of the time okay in low temperature; by the 300 Kelvin room temperature you are little bit on the borderline, you know. We start seeing signatures like in QR branch of where one sees in vibrational spectra the rotational level dependence and that has been enormously important study in 1980s that to see the rotational level dependence of vibrational or electronic relaxation, that was a big, big thing in those days, you know it is considered to be.

So remember the Nobel prize Ahmed. H. Zewail got in 1998, there is a for his exponential result done 1987, he used many of these things to establish certain reaction pathway. Okay so we if we now assume that these things are independent of each other rotation, vibration, electronic independent of each other that is an approximation.

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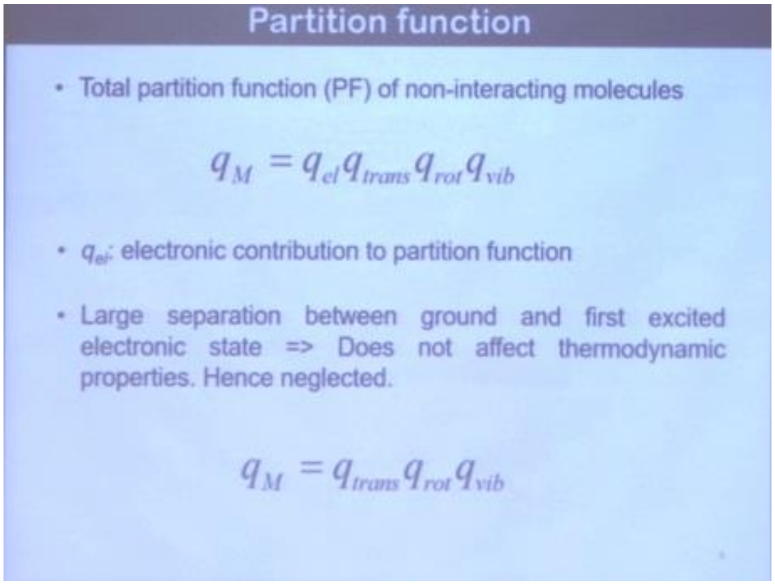

Partition function

- Total partition function (PF) of non-interacting molecules

$$q_M = q_{el} q_{trans} q_{rot} q_{vib}$$

- q_{el}: electronic contribution to partition function
- Large separation between ground and first excited electronic state => Does not affect thermodynamic properties. Hence neglected.

$$q_M = q_{trans} q_{rot} q_{vib}$$

Yes. Rotational; there is a very good question that can also come but that is can come by the way for example if a large-scale collision then you can have a coupling between rotation and translation but in usually that is weaker than the rotation, vibration rotation coupling. Okay, now so if they are in non-interacting and they are independent then total molecular partition function q_M stands for molecule.

$$q_M = q_{el} q_{trans} q_{rot} q_{vib}$$

Molecular partition function is a product of the individual partition functions that because if they are independent the energy levels of each are different and partition function is some of the energy levels. You understand that? Okay, q is sum over e to the power - Ei /k_B T and this part I think I will probably remind you a few times because this we have not done properly or in great detail.

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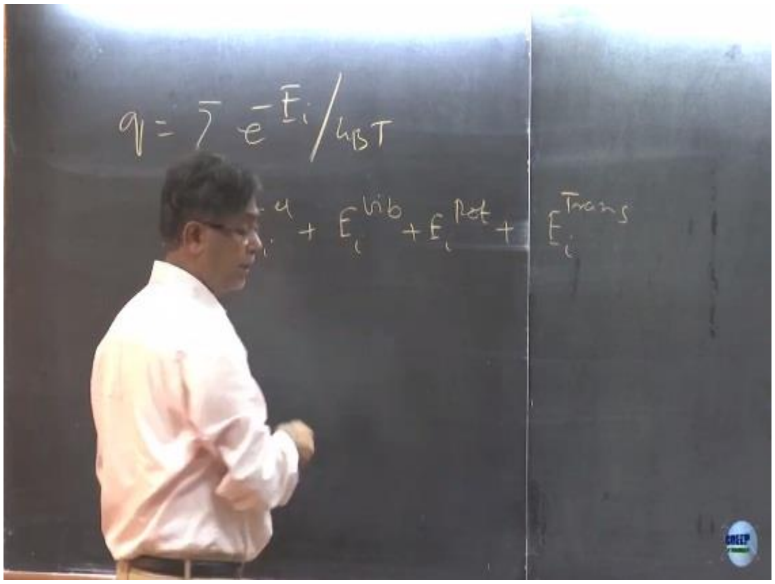

So partition function if I say q notation then e to the power - Ei / k_BT which meant constant, now sum over I, now see if Ei depends on Ei electronic + Ei vibration + Ei rotation + Ei translation then you go sum then you separate them out because these goals in the exponent; this all becomes, all becomes product. So this is then a non-interacting molecular, molecular partition function.

Now the important thing is that electronic energy levels, now I have asked you a question that what is the typical electronic energy levels in molecules and how does it compare with the vibration, rotation, and translation? Let us start with translation. What is the energy gap between two if I do quantum mechanics, then I get that, that particle in a box. Give me a number, what is the typical number of energy levels spacing between two translational energy levels?

These can kind of tells either you think at all or not. See you have one all of these things, you are doing statistical mechanics and you should be able to tell what is the energy level, what is gap in translation, say loudly. So many of you should make at least one guess, it is okay to be wrong, but you should have some guess. Still okay, I give you one number room temperature 1 k_BT is 206 cm^{-1} then how many centimeter inverse?

That is what experiment please do and I want to log in an experiment how much? Okay, 10 cm^{-1}, that is a good guess. How much the rotation? **“Professor - student conversation starts”** How much more? That is actually correct no much more than about say 100 or maybe 50; depending on the moment of inertia. Now vibration, what is the energy levels in vibration, molecular vibration. This you guys should do because this we did a lot in undergraduate.

What is a vibrational gap between vibration energy level say from nitrogen or oxygen? Exactly 3600 cm^{-1}, one is symmetric stretching is 3660 and asymmetric stretching is 3700 cm^{-1}. How much is bending, OH bending? You said something correct, next one. Very important, the average bending that plays a very important role in your body. So I will ask you; show I will continue I come back to it “**Professor - student conversation ends.”**

So translation is much less than k_BT, so at normal temperature translation is like a continuum, rotation is your borderline low temperature it also discrete or high temperature is continuum, vibration if it is asymmetric stretching 3700, bending is 1885 then that is about 10 bending is 10 but others are typically 15 to 20 times, so that is absolutely quantum.

How much is electronic energy levels? See you cannot compute; you will not be able to talk with an experimentalist if you do not know these basic things, that is what they are doing all the time in IR, FTIR, NMR all the things. How much is electronic energy levels? More than 10,000 cm^{-1}. So 10,000 centimeter inverse means you have something 50 k_BT or so.” Professor to student conversation ends

So gap between ground state and excited state is that huge amount that is why they does not have; there is no population at normal temperature in the excited electronic state. Everything happening in the ground state then we do not need to carry this ground. This is also the reason when the solid state physicists; let us not talk about solid state I do not know how much they really follow things.

Solid state physicists never bother about temperature. They do not need to do statistical mechanics for much of the time. The reason because that, when they talk, they are talking of the excited electronic excitation much of the time, so they are talking of this huge energy gap, okay.

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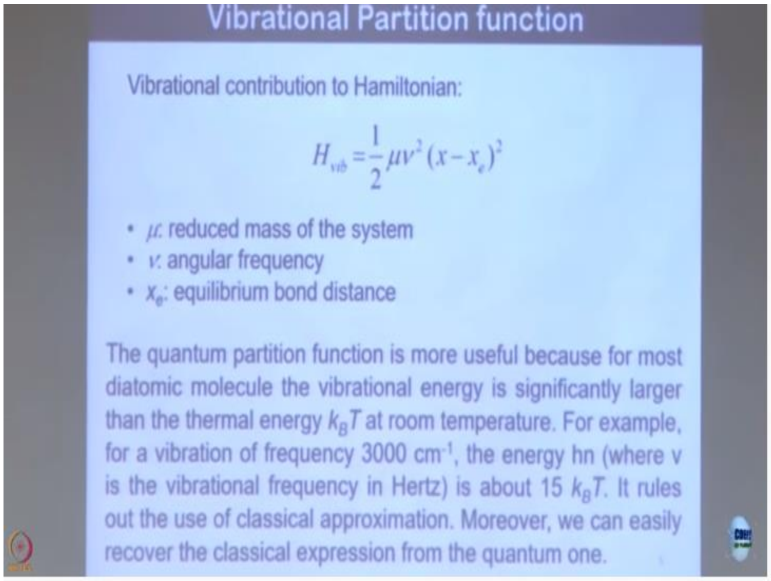

Vibrational Partition function

Vibrational contribution to Hamiltonian:

$$H_{vib} = \frac{1}{2}\mu v^2 (x - x_e)^2$$

- μ: reduced mass of the system
- v: angular frequency
- x_e: equilibrium bond distance

The quantum partition function is more useful because for most diatomic molecule the vibrational energy is significantly larger than the thermal energy k_BT at room temperature. For example, for a vibration of frequency 3000 cm^{-1}, the energy hn (where v is the vibrational frequency in Hertz) is about 15 k_BT. It rules out the use of classical approximation. Moreover, we can easily recover the classical expression from the quantum one.

$$H_{vib} = \frac{1}{2}\mu v^2 (x - x_e)^2$$

Let us now do vibration also. So we have to do it quantum then we have done translation, translation what remains the same as we did in the morning then we do vibration then we do rotation, okay. So this is a half Mu square, x - x e square, so this is n l square and this frequency 1 over T square so this is an energy nl square/T square. It is reduced mass of the system in this case says that you know I am going to 1 degree reduction of degree of freedom, that means the my a is this is my reaction my coordinate. Now we have to solve this. Now tell me how we will go about it now? Here I say 3000 centimeter, 15k $_B$T all the numbers are there. Now tell me one thing how do I go about it now?

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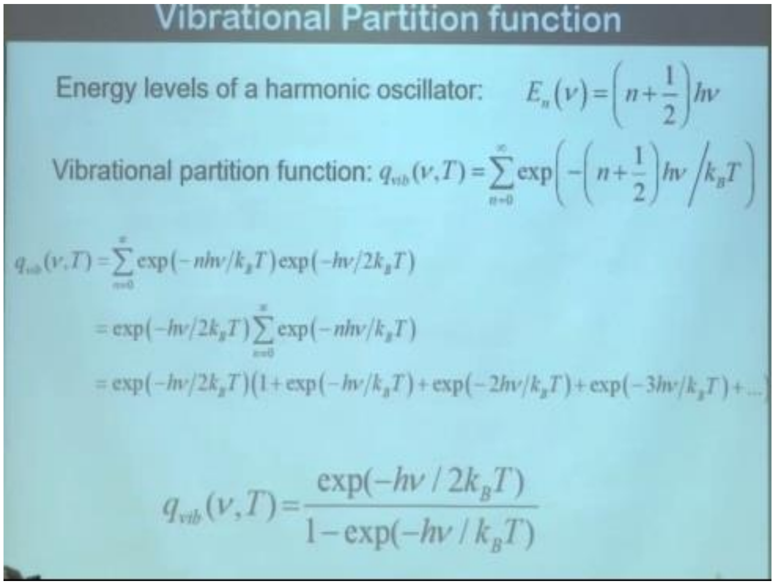

Vibrational Partition function

Energy levels of a harmonic oscillator: $E_n(\nu)=\left(n+\frac{1}{2}\right)h\nu$

Vibrational partition function: $q_{vib}(\nu,T)=\sum_{n=0}^{\infty}\exp\left(-\left(n+\frac{1}{2}\right)h\nu\Big/k_BT\right)$

$$q_{vib}(\nu,T)=\sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)\exp(-h\nu/2k_BT)$$

$$=\exp(-h\nu/2k_BT)\sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)$$

$$=\exp(-h\nu/2k_BT)(1+\exp(-h\nu/k_BT)+\exp(-2h\nu/k_BT)+\exp(-3h\nu/k_BT)+\dots)$$

$$q_{vib}(\nu,T)=\frac{\exp(-h\nu/2k_BT)}{1-\exp(-h\nu/k_BT)}$$

Okay. The way I go about it is I solve the quantum problem schrödinger equation and this is the energy levels. This part all of you have done many times, okay. And then vibrational partition function there is just sum over these things; is sum n from 0 that is a big difference, 0 to infinity, okay. If n = 0 to infinity, then this quantity half hv/ k_BT. I guess certainly here and there some mistakes we have to find mistakes; I asked my student to; this there is a two missing here, why he went to write these things I do not know I should have guessed.

$$q_{vib}(\nu,T)=\sum_{n=0}^{\infty}\exp(-(n+\frac{1}{2})h\nu/k_BT)$$

$$q_{vib}(V,T) = \sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)\exp(-h\nu/2k_BT)$$

$$= \exp(-h\nu/2k_BT)\sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)$$

$$= \exp(-h\nu/2k_BT)\,[1+ \exp(-h\nu/k_BT) + \exp(-2h\nu/k_BT) + \exp(-3h\nu/k_BT) +\dots\dots]$$

Okay there should be n + 1/2 hv so E to the power – 1/2 hv / k_BT come out. I remember this side we need to change, okay. And then these goes out and then we sum n = 0 to infinity e to the power – nhv / k_BT. Now this sum can be done and tell me what is this sum? This is the energy level, so I have divided k_BT like Ei / k_BT, this is the thing that is here, so e to the power -; does not have any end, it comes out that comes out here.

Actually that should come in front actually okay, but we can leave with that because that has no end then I have brought it here then I have to sum n = 0 to infinity to my nhv / k $_B$T. So this now n = 0, so n = 0 is 1 then this now into your –hv; is x, okay. So you 1 + x + x square + x cube that is the geometric progression and then that is equal to 1 over 1-x and x is e to the power – hv /k $_B$ T so this quantity comes here.

$$q_{vib}(\nu,T)=\frac{\exp(-h\nu/2k_BT)}{1-\exp(-h\nu/k_BT)}$$

So we have; but these are very beautiful reserve, really nice is that. The vibration of partition function e to the power - hv / 2 k $_B$T is very pretty. Okay. And this is the one we will discuss more about it, okay. Good that we corrected it.

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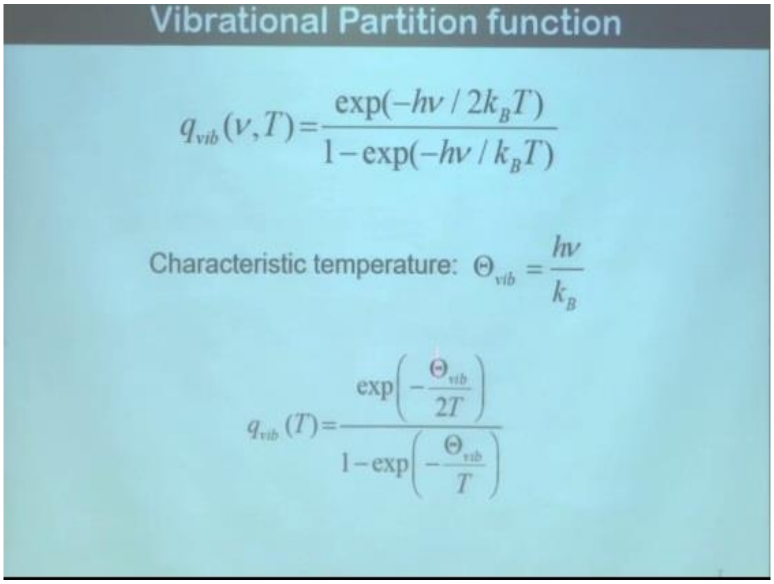

Vibrational Partition function

$$q_{vib}(\nu,T)=\frac{\exp(-h\nu/2k_BT)}{1-\exp(-h\nu/k_BT)}$$

Characteristic temperature: $\Theta_{vib}=\dfrac{h\nu}{k_B}$

$$q_{vib}(T)=\frac{\exp\left(-\frac{\Theta_{vib}}{2T}\right)}{1-\exp\left(-\frac{\Theta_{vib}}{T}\right)}$$

So again the fully bolded equation. Now this defines the temperature, which is also the one actually done by Debye. So now hv / 2k $_B$T this kind of game I rewind by theta vibration show, see these quantity hv/k $_B$ has the dimension of temperature because exponential has to be dimensionless, so I define as the vibrational temperature and vibrational temperature as I said would be 10, 15 or 20 times the normal temperature, okay. So theta vibration by 2T, 1 – e to the power theta vibration by T. Okay.

$$q_{vib}(T) = \frac{\exp\left(-\frac{\Theta_{vib}}{2T}\right)}{1-\exp\left(-\frac{\Theta_{vib}}{T}\right)}$$

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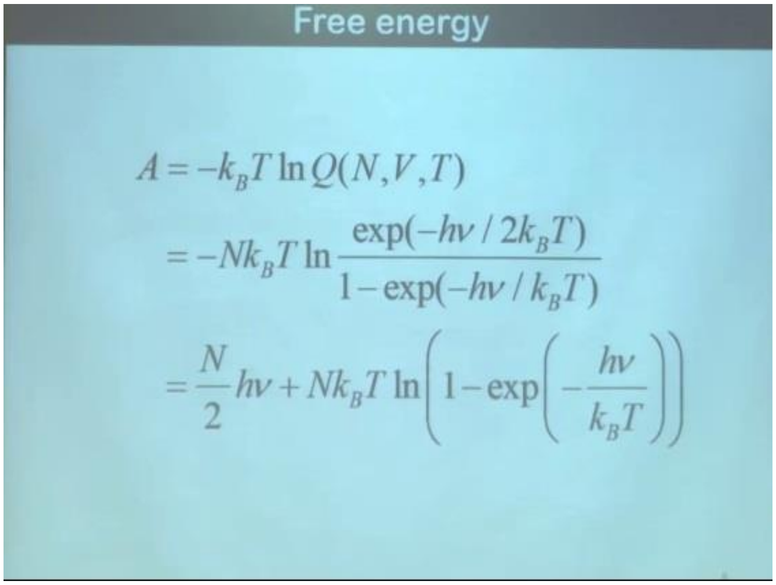

Free energy

$$A = -k_B T \ln Q(N,V,T)$$
$$= -Nk_B T \ln \frac{\exp(-h\nu/2k_B T)}{1-\exp(-h\nu/k_B T)}$$
$$= \frac{N}{2}h\nu + Nk_B T \ln\left(1-\exp\left(-\frac{h\nu}{k_B T}\right)\right)$$

Now we; from this now we are going to go this is the form which this is the form which I did while doing this specific term and we might come back to that. Now, so free energy I know there is a canonical partition function free energy. Now let us again slightly go back let me repeat how we did this calculation. We are going to calculate the canonical partition function. We have a system that characterize by N, V, T.

And then the quantum mechanics giving us the energy levels. In classical system quantum mechanics gives up the force field, that what you guys use, that the particle interact with Lennard Jones parameters where initially obtain from experiments were fitting, they found the small a and small b of Van der waals parameters and the Lennard Jones, Lennard Jones actually found it what we as it name.

So either experiment or quantum calculations give me the potential force field. Here quantum calculation will give me these quantities and this mass we know but these are the quantum rules. Once quantum gives us that with the assumption of, we get the energy levels.

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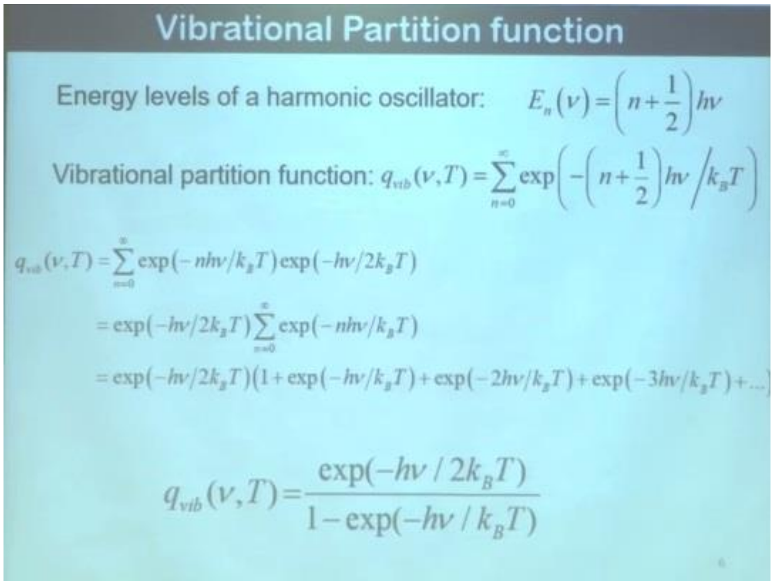

Vibrational Partition function

Energy levels of a harmonic oscillator: $E_n(\nu) = \left(n + \frac{1}{2}\right)h\nu$

Vibrational partition function: $q_{vib}(\nu, T) = \sum_{n=0}^{\infty} \exp\left(-\left(n + \frac{1}{2}\right)h\nu \Big/ k_B T\right)$

$$
\begin{aligned}
q_{vib}(\nu, T) &= \sum_{n=0}^{\infty} \exp(-nh\nu/k_B T)\exp(-h\nu/2k_B T) \\
&= \exp(-h\nu/2k_B T)\sum_{n=0}^{\infty} \exp(-nh\nu/k_B T) \\
&= \exp(-h\nu/2k_B T)(1 + \exp(-h\nu/k_B T) + \exp(-2h\nu/k_B T) + \exp(-3h\nu/k_B T) + \ldots)
\end{aligned}
$$

$$q_{vib}(\nu, T) = \frac{\exp(-h\nu / 2k_B T)}{1 - \exp(-h\nu / k_B T)}$$

Once we get the energy levels, we are now going to get the vibrational partition function and here we get temperature T is there, okay. Now, and then these follows. So now this canonical partition function has the temperature unit.

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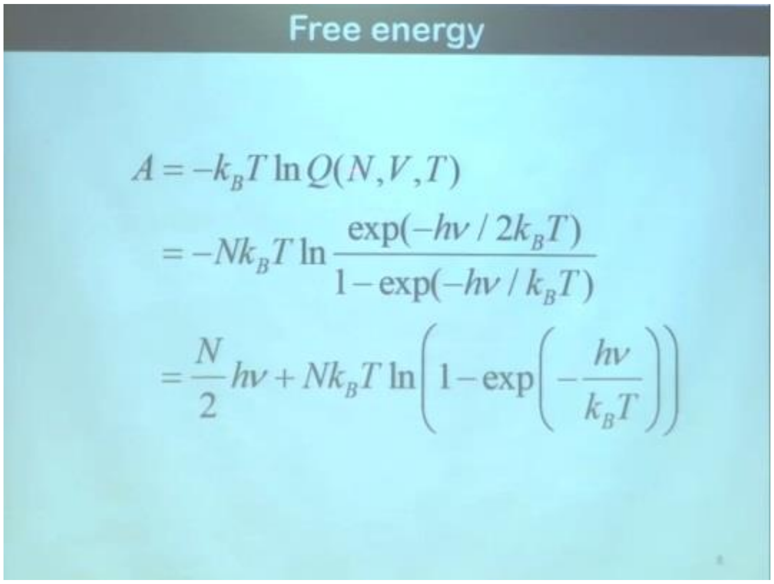

Free energy

$$
\begin{aligned}
A &= -k_B T \ln Q(N, V, T) \\
&= -Nk_B T \ln \frac{\exp(-h\nu / 2k_B T)}{1 - \exp(-h\nu / k_B T)} \\
&= \frac{N}{2}h\nu + Nk_B T \ln\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right)
\end{aligned}
$$

We are now going to calculate the free energy.; now the vibration this a single one vibration but if there are n number of vibration then what will happen, we have discussed in many times now you should be able to tell me, if I have n number of; for non-interacting harmonic oscillators? Exactly will be the same and they will be to the power n, right.

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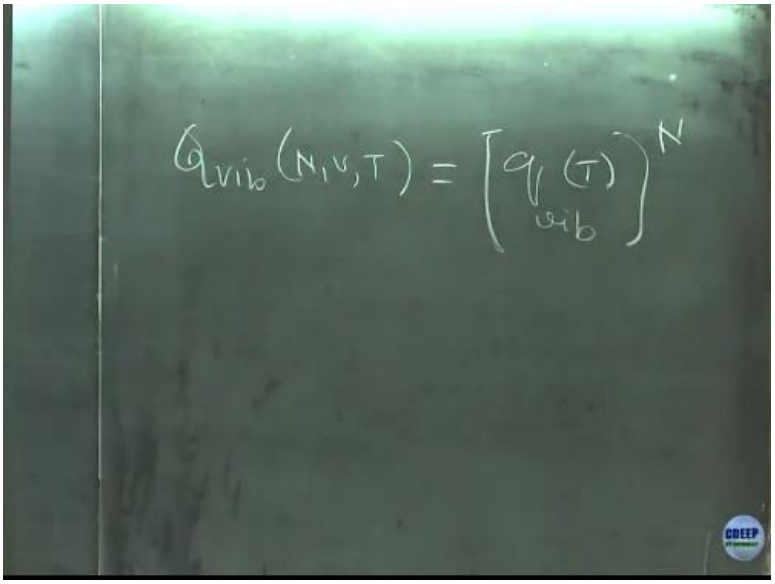

$$Q_{vib}(N,V,T) = \left[q_{vib}(T)\right]^N$$

So capital Q vibration in N, V, T is q vibration, okay. So if that is the case then ln Q that Q n comes in front N k $_B$T ln this quantity. Now a - sign is there - sign is here, so now these are two logarithmic terms I take that though in the first term this one I get N/2 hv, k $_B$T,k $_B$ T cancels, second one Nk $_B$T remains since in the denominator - and - gets cancelled then I get 1-; so this is the canonical partition function of n number of harmonic oscillators.

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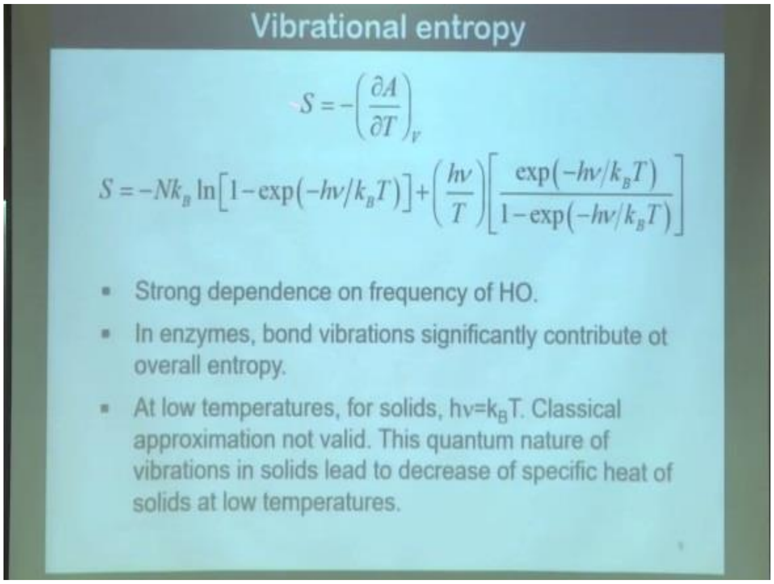

Vibrational entropy

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

$$S = -Nk_B \ln\left[1-\exp\left(-h\nu/k_BT\right)\right] + \left(\frac{h\nu}{T}\right)\left[\frac{\exp\left(-h\nu/k_BT\right)}{1-\exp\left(-h\nu/k_BT\right)}\right]$$

- Strong dependence on frequency of HO.
- In enzymes, bond vibrations significantly contribute ot overall entropy.
- At low temperatures, for solids, $h\nu = k_BT$. Classical approximation not valid. This quantum nature of vibrations in solids lead to decrease of specific heat of solids at low temperatures.

Now I get to go to entropy is –dA/dT and S and - from where I take the derivative dA dT, this guy has no temperature dependence. And by the way what is, where this term coming from? Please tell that that, where is this term coming from? It is a very important where this term coming from. It is 0, no it is 0 vibrational level, the famous 0th vibration energy which saves the uncertainty principle. So even at 0 Kelvin these motion remains, this is amazingly important, so it is the 0 vibration energy level.

Okay that is this term, that is no temperature dependent, so that term drops out and so now let us do this, this I have to do temperature derivative one is just Nk_BT ln this term next term Nk_BT then just like within translational case we take then that comes as 1 over - this thing then I go inside and take derivative of that and that then give me 1; I recover again e to the hv / Nk_BT – is a plus another - from 1/T derivative so that -1 over T Square, okay.

And now I take that T out here and there was a T in front here so that T and T Square here gives me this T here hv/T because that comes from derivative and then this is the quantity because I said we bring that here and three negatives makes it negative, that negative comes here. Okay. So these; then when you do this derivative come here you do again the derivative you say this is just Nk_B ln in this term and then derivative this term comes in denominator so then this term plus this term, okay. So this is the expression of entropy.

So one important very important thing is that they have a very strong dependence on the frequency of the harmonic oscillators because it is an exponent everywhere. Entropy is strongly dependent on the vibrational frequency, which is a very important thing. Because, since nu is large in have to be in molecular cases this does not contribute much to thermodynamics. So many times in our calculations we do not take vibration into account, when you are doing simulation of water you do SPCE at Tip4P, but you do not have vibration there.

On any other systems we just do not that just because this is the reason. However, when you have big proteins they have many vibrational modes which are low frequency which are conformational vibrations; DNA, enzymes, proteins or even you know when you are looking or low temperature glasses there are these; so at low temperature for solids this becomes classical approximation but quantum nature of vibration leads to decrease in this specific heat this is the famous.

Remember lowering up specific heat into the temperature; what is the asymptotic; what is the Dulong–Pettit's law? Dulong–Pettit's law tells this specific it of a solid is equal to 3R, are very, very good 3R. 3/2 comes from term a and translational 3/2 vibration, okay. We will derive that in a minute but what Einstein tried to explain that high temperature it goes to Dulong–Pettit's law 3R, but low temperature it deviates significantly, that was among many other things signature of quantum mechanics.

Einstein did one more signature of quantum mechanics what is that? Photoelectric effect which started of course with planks, right blackbody radiation, blackbody radiation also these vibrations are involved because electromagnetic wave okay.

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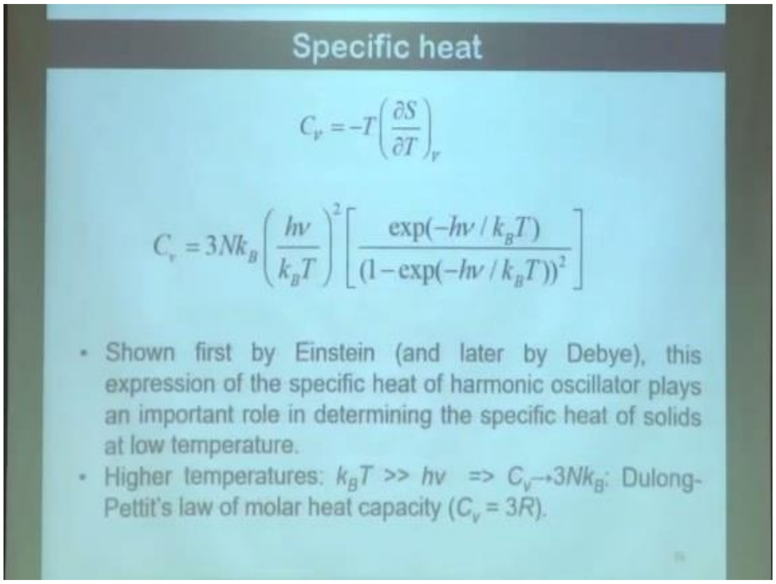

Specific heat

$$C_v = -T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2\left[\frac{\exp(-h\nu / k_BT)}{(1-\exp(-h\nu / k_BT))^2}\right]$$

- Shown first by Einstein (and later by Debye), this expression of the specific heat of harmonic oscillator plays an important role in determining the specific heat of solids at low temperature.
- Higher temperatures: $k_BT >> h\nu$ => $C_v \to 3Nk_B$: Dulong-Pettit's law of molar heat capacity ($C_v = 3R$).

Now you do this Specific heat. Specific heat this quantity just we did before, so here we have to take the derivative of these quantities now it is getting little complicated, they are not as simple as translation, but we would be able to take that like dS/dt you know, again this guy comes below then I take the derivative and that becomes then e to the power -hv / k $_B$T and then and outside comes -hv /k $_B$ T square - another - comes here as I said you -, -, - it becomes -, 4 minutes it becomes positive and then you take derivative of this things very fairly complex.

You have to take derivative of this, that being – 1 over T T square and then you have to take derivative of this guy then again that same game - and - plus hv / k $_B$T Square and then you have this quantity which you also have to take the derivative that then it becomes a squared here because a denominator then you take the derivate of that that when you do all these things, you get; that square comes here and so this is finally combining everything; this beautiful expression comes in.

$$\boxed{C_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2\left[\frac{\exp(-h\nu/k_BT)}{(1-\exp(-h\nu/k_BT))^2}\right]}$$

So this is a specific heat of a bunch of harmonic oscillators which is so important in solids because solids remember normal modes. Now what are the normal modes in solids? What are the normal modes in solids? How do we get normal modes in solids? Right, yeah absolutely, that is called dynamical matrix you are like that x1 – x2 square + x2 – x3 square, so x1 - x2; x2 – x3, x4 they are all coupled but x1 and x2 are the positions instead if I make the transformation that is x1 - x2 is the coordinate so it is called displacement coordinate.

Then you can decouple and is formally done by introduce what is the dynamical matrix say transformation. Then it becomes a bunch of harmonic oscillators and the eigenvalues are the harmonic frequencies and eigenvectors are the modes. So solid state, much of solid state can be described as thermal properties not the electronic properties, thermal properties of solids can be described and that is what Einstein and Debye did. So shown by Einstein literally divided these expressions specific heat of harmonic oscillator plays an important role in determining specific of solid.

It continued to play very important role, you know and the guy who great got noble prize for other things Philip Anderson famous theory of showing that at a very low temperature this one shows an exponential dependence that does not work out Debye corrected it by saying that Einstein assumed only one; there is a beautiful work he said, whole solid has one frequency that is Einstein did he said these expression. Debye says, no that is not possible because there is a distribution and also there is upper limit; when we induce that fact, he caught T cube law.

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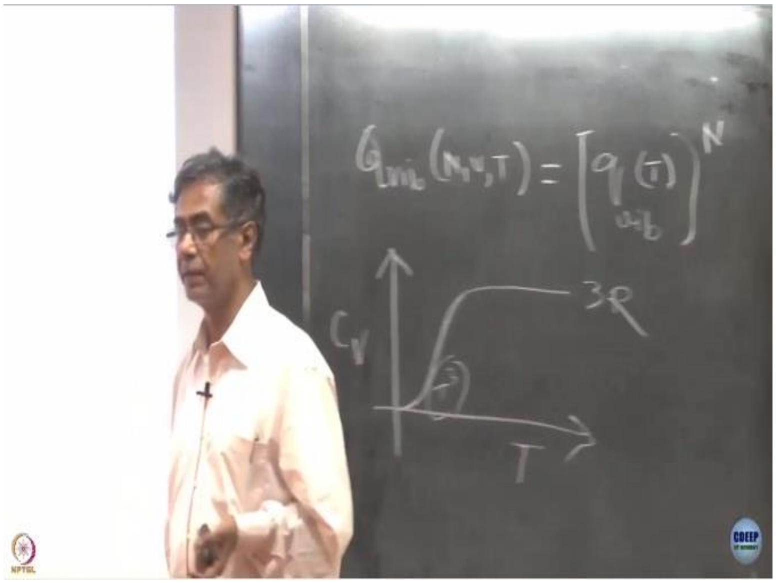

So specific heat of solids, so it goes like that; this is 3R Dulong–Pettit's law. Here it you find some signature of exponential but here it goes as T cube; that is the one that Debye corrected by improving on Einstein's assumption of single mode. However, from now look at that you take the case that I go to high temperature in this region, this region here; this is the one I am going to look at now okay and that is by when temperature is large then Cv you can look at that take the large temperature then it goes to 1, you expand this one because this is hv / k $_B$T small, okay. I expand that I call; we already called it x1 before we can call x1 or more.

So then e to the power - x, I expand 1 - x – x; and + x square, so the 1 cancels 1, I keep the lowest order term which is x; there is a square here it becomes x square and that then cancels this because hv/k $_B$T and then Cv is 3k $_B$B, okay. So which is nothing but 3R, so high temperature this beautifully goes over to Dulong–Pettit's law. This is an amazingly very pretty, very pretty part of statistical mechanics, that as I told you in the morning that we get ideal gas law.

We get the PV = RT; we get Cv = 3/2R, so all these things we get; we get this Sackur–Tetrode equation. But now we are seeing that it is a huge thing in; we are explaining the properties of the specific heat of solids which are they know must be important and experiment to be observed for you.